

UC Irvine

UC Irvine Previously Published Works

Title

Seasonal variation of tropospheric methyl bromide concentrations: Constraints on anthropogenic input

Permalink

<https://escholarship.org/uc/item/0297x831>

Journal

Geophysical Research Letters, 25(15)

ISSN

0094-8276

Authors

Wingenter, OW
Wang, CJL
Blake, DR
et al.

Publication Date

1998-08-01

DOI

10.1029/98GL02179

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Seasonal variation of tropospheric methyl bromide concentrations: Constraints on anthropogenic input

Oliver W. Wingenter¹, Charles J.-L. Wang², Donald R. Blake and

F. Sherwood Rowland

Department of Chemistry, University of California, Irvine, California

Abstract. Although removal of tropospheric methyl bromide (CH_3Br) is dominated by the reaction with the seasonally varying hydroxyl (HO) radical concentration, the anticipated corresponding seasonal dependence of CH_3Br , as found for other gases with major HO sinks, has been sought previously without success [WMO, 1995]. Our observations of northern hemispheric boundary layer CH_3Br concentrations do reveal substantial seasonal changes. The high latitude CH_3Br North/South interhemispheric concentration ratio (IHR) varies from a maximum of 1.35 ± 0.04 (1σ) in March-April to 1.10 ± 0.04 in September, with an equal area and seasonally (EAS) weighted average IHR of 1.21 ± 0.03 . These observations suggest northern hemispheric emissions are about 15 kilotons/year less than when an IHR of 1.3 is considered [WMO, 1995]. The observed seasonality also partially explains the differences in the IHR reported by several research groups [WMO, 1995] and places needed constraints on the magnitude and seasonality of sources and sinks of CH_3Br .

Introduction

Methyl bromide, with a global atmospheric mixing ratio of about 9 pptv (parts per trillion by volume), accounts for about half of the total carbon-bonded bromine in the troposphere [WMO, 1995]. Bromine monoxide (BrO) radicals react very quickly with chlorine monoxide (ClO) and hydroperoxy (HO_2) radicals, contributing significantly to stratospheric ozone loss. The quantitative evaluation of the various contributions to the atmospheric emissions and removal processes for CH_3Br is particularly complicated because of its multiple sources (oceanic [WMO, 1995], biomass burning [Blake, D. R. *et al.*, 1993; Manö and Andreae, 1994] anthropogenic [WMO, 1995; Yagi, *et al.*, 1995] and sinks (HO [WMO, 1995], oceanic [Yvon, *et al.*, 1996], soil [Shorter, *et al.*, 1995])).

Within a three week period in every season since 1983, our research group has been collecting 60 to 80 whole air samples in evacuated 2-liter stainless steel canisters throughout the remote Pacific from Barrow, Alaska (71°N), to Bluff, New Zealand (47°S). During each collection period, approximately 12 air samples from Alaska (Barrow to Kodiak, 57°N), and 10

samples from various locations on the New Zealand coast (37°S to 47°S) were returned to the University of California, Irvine (UCI) for hydrocarbon and halocarbon analysis by gas chromatography. In 1992 CH_3Br was added to our routine analysis. Experimental procedure, standardization, precision estimates and chromatographic information are given elsewhere [Wang, 1993; Blake, D. R. *et al.*, 1996].

CH_3Br Seasonal Variability

The March 1995 CH_3Br latitudinal profile in Figure 1 illustrates the typical concentration variability found at remote sites. In four samples collected between 30° and 40°N the CH_3Br concentrations were substantially enhanced compared to background levels. These four samples were also enhanced in urban and/or combustion emissions and were therefore removed, along with similarly augmented samples from the other collections, from IHR and other calculations. Samples collected along the U.S. West Coast are occasionally affected by mixing of air parcels influenced by urban, combustion and fumigation emissions.

Average background concentrations in Alaska and the northern hemisphere (NH) from the March period and 5 other seasonal collections (Table 1 and Figure 2) can be fitted sinusoidally (R^2 values of 0.96 and 0.98, with peak to valley amplitudes of 2.5 pptv and 1.5 pptv for Alaska and the NH, respectively). The phase is consistent with strong seasonal removal by HO. Also contributing to additional summertime losses are the strong positive temperature dependencies of CH_3Br toward nucleophilic substitution and hydrolysis in

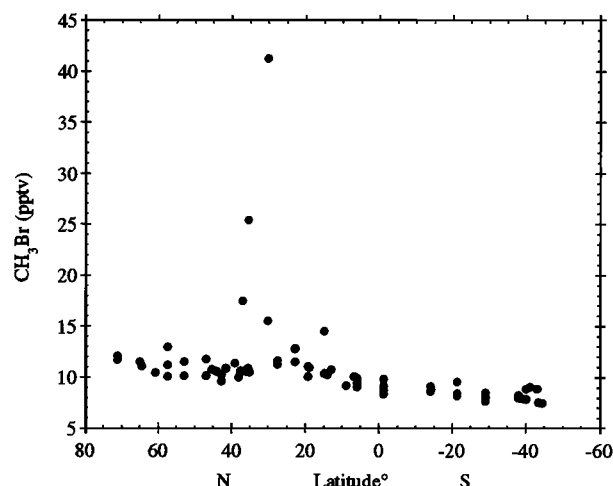


Figure 1. March 1995 methyl bromide latitudinal profile.

¹Now at the Georgia Institute of Technology, Georgia.

²Now at the National Central University, Chung-Li, Taiwan.

Table 1. Average Methyl Bromide Concentrations in Surface Samples Collected in Alaska and New Zealand and their Ratios (AK/NZ IHR). Also the Average Hemispheric Concentrations, Equal Area Interhemispheric Ratio (EA IHR) and Global Averages Weighted on an Equal Area Basis. Errors are One Standard Deviation of the Mean. Mixing Ratios are in pptv.

Date	Alaska	New Zealand	AK/NZ IHR	NH ave	SH ave	Global ave	EA IHR
4/92	10.2±0.3	7.5±0.4	1.35±0.05	10.1±0.2	8.0±0.3	9.0±0.3	1.26±0.03
8/92	8.8±0.2	7.7±0.2	1.15±0.03	9.1±0.4	7.8±0.2	8.5±0.3	1.17±0.04
6/94	9.5±0.2	7.8±0.2	1.21±0.03	9.6±0.3	7.9±0.3	8.7±0.3	1.22±0.04
9/94	8.7±0.2	7.9±0.3	1.10±0.04	9.5±0.3	8.1±0.4	8.8±0.4	1.18±0.05
12/94	10.7±0.3	8.4±0.3	1.28±0.05	10.6±0.4	8.7±0.2	9.6±0.3	1.22±0.04
3/95	11.1±0.2	8.2±0.2	1.35±0.03	10.5±0.2	8.4±0.3	9.5±0.3	1.24±0.03

ocean water [Elliott and Rowland, 1993; Elliott and Rowland, 1995], and biological uptake in soil [Shorter, *et al.*, 1995]. Agricultural usage of CH_3Br at lower latitudes occurs during the growing season which may contribute to the higher IHR observed in September for the NH average when compared to the Alaskan average. The relatively lower NH March average is consistent with hemispheric dilution and diminished high latitude losses [Blake and Rowland, 1986; Wang, *et al.*, 1995].

The absence of any pronounced seasonal variation of CH_3Br concentrations in New Zealand or the southern hemisphere (SH) (Table 1 and Figure 2) implies the SH must have one or more seasonal influences out of phase with HO removal. Marine production of CH_3Br is at times closely associated with chlorophyll levels [Anbar, *et al.*, 1996], which satellite observations indicate have the greatest activity in summer [Feldman, 1989]. Cool summertime Southern Ocean temperatures coupled with high chlorophyll production [Comiso *et al.*, 1993] could lead to large summertime CH_3Br emissions at high southern latitudes [Anbar *et al.*, 1996]. However, the few observations made in this region do not support this hypothesis. On the contrary, during a cruise from

21 February to 7 April 1996, originating from McMurdo, Antarctica, to Punta Arenas, Chile, this portion of the Southern Ocean was undersaturated in CH_3Br [Lobert *et al.*, 1997]. Under similar conditions in the Northwest Atlantic, cold Northwest Atlantic waters with high chlorophyll concentrations were encountered during July, and the region was undersaturated in CH_3Br [Moore and Webb, 1996]. Because the SH land area is 1/3 as large as that of the NH, the soil sink should contribute much less to summertime losses there. Largely seasonal CH_3Br emissions from South American and southern African biomass fires further complicates the southern temperate source and sink signal [Blake *et al.*, 1993; Manö and Andreae, 1994; N. J. Blake *et al.*, 1996; Fishman *et al.*, 1996].

CH_3Br Interhemispheric Ratios

The CH_3Br IHRs from six of our collection periods are given in Table 1 and the Alaska/New Zealand (AK/NZ) IHRs are shown in Figure 3. In the past, IHR ratios have been used for intercomparisons among data from various research groups in order to bypass the separate problem of uncertainties in absolute calibration. These IHR values are not from equivalent locations or seasons, and "consensus" values for IHR have been used to estimate the percent anthropogenic component of CH_3Br emissions [WMO, 1995]. Between 1985 and 1987 Cicerone *et al.* [1988] collected about 6 samples per month from Point Barrow, Alaska, and 4 per month from Kaitorete Spit, New Zealand (44° S). These were subsequently analyzed for CH_3Br by gas chromatography/mass spectrometry, and are plotted in Figure 3 as 12 monthly IHR averages. Our own AK/NZ IHRs and those of Cicerone *et al.* exhibit a seasonal variation, with a maximum in late boreal winter, and a minimum in late boreal summer. Separate sine curve fits to these two data sets have very similar parameters. After weighting each set equally they were combined and a single curve was fit (Figure 3). Taking the range and uncertainty from the curve, the maximum IHR is 1.34 ± 0.03 (1σ) in March and the minimum is 1.07 ± 0.03 in September with a seasonal average of 1.21 ± 0.03 . Five other data sets [Groszko and Moore, in press; Singh *et al.*, 1983; Schauffler *et al.*, 1993; Penkett *et al.*, 1985; Singh and Kanakidou, 1993] collected over short time periods by different research groups are also

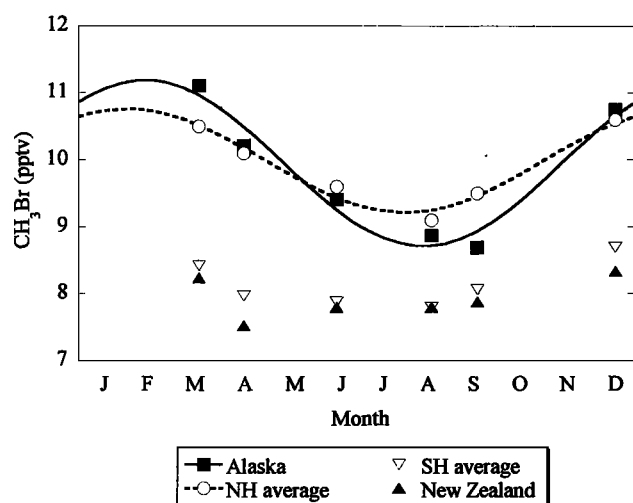


Figure 2. Seasonal concentrations of CH_3Br in the Northern and Southern Hemispheres, Alaska and New Zealand.

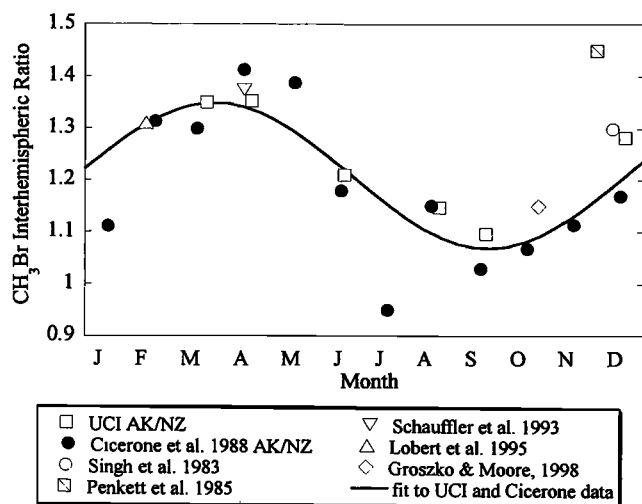


Figure 3. Seasonal variation of methyl bromide IHR. The curve was fit to Cicerone *et al.* and UCI data only.

shown in Figure 3. The Schauffler *et al.* IHR [WMO, 1995; Schauffler *et al.*, 1993] was determined from their April 1993 Pacific cruise, using data north of 45° N and between 37° S and 60° S. The IHR reported by Penkett *et al.* [1985], who collected samples in the Atlantic, deviates significantly from the seasonal variation evident in Figure 3 and is likely influenced by recent continental emissions [Blake, D. R. *et al.*, 1996]. The entire composite data set of Figure 3 suggests that much of the apparent past disagreement in the IHR, as reflected in the previous error estimate of ± 0.15 [WMO, 1995] resulted from the comparison of data taken in different seasons.

Averaging our 1994–1995 data over all latitudes on an equal area and seasonal (EAS) basis [Wang, 1993] (Table 1), our global CH₃Br mixing ratio estimate during the 1994–1995 period is 9.2 ± 0.5 pptv with a peak to valley amplitude (taken from the curve) of 1.1 pptv (R^2 is 0.99). The hemispheric emissions needed to sustain the derived 1.21 ± 0.03 EAS IHR were studied using a simple two box model representing the NH and SH employing an exchange time of 1.2 years. The model assumes an average annual HO lifetime of 1.7 y [WMO, 1995], oceanic [Yvon and Butler, 1996] and soil [Shorter *et al.*, 1995] lifetimes of 2.7 y and 3.4 y respectively, yielding a total CH₃Br lifetime of 0.8 y, with total emissions of 185 kilotonnes/year (kt/y) [Singh and Kanakidou, 1993]. Previously, CH₃Br sinks and non-industrial sources were assumed to be nearly evenly distributed between the NH and SH [WMO, 1995; Reeves and Penkett, 1993; Butler and Rodriguez, 1996] with industrial emissions (all assumed to occur in the NH) responsible for the IHR being greater than unity. In order for the model to predict an IHR of 1.21, emissions of 114 kt/y in the NH and 71 kt/y in the SH are necessary; in other words 42 kt/y more or extra NH emissions are needed for this IHR. Predicting the WMO [WMO, 1995] estimated IHR of 1.3 requires extra NH emissions of 57 kt/y. Therefore, when compared to a seasonally and area weighted IHR of 1.21, a 1.3 IHR overestimates NH emissions (and thus industrial emissions) by 15 kt/y.

The assumption that all non-industrial emissions are evenly distributed between hemispheres is plausible, but is neither supported nor negated by observation. We have therefore also

calculated the effects on the estimate of industrial emissions with alternate initial assumptions. In addition to the 50 percent non-industrial emission case, model runs for 40 and 60 percent of the total NH non-industrial CH₃Br emissions were also calculated. When compared to our 1.21 IHR, the 1.3 IHR over predicts NH emissions by 13 and 19 kt/y respectively, for the 40 and 60 percent scenarios. The assumption that all sinks are symmetric about the equator was also tested and two scenarios were run. Sink strengths were increased 10 percent in the NH and decreased 10 percent in the SH in the first scenario, while in the second the NH sinks strengths were decreased 10 percent while the SH sink strengths were increased 10 percent. In the first case the extra NH emissions for the 1.21 IHR were 61 kt/y, while the 1.3 IHR required extra NH emissions of 75 kt/y, 14 kt/y more than predicted for a 1.21 IHR. For the second case 24 kt/y extra NH emissions were required to sustain a 1.21 IHR, whereas the 1.3 IHR required 40 kt/y extra NH emissions per year, 16 kt/y more than the 1.21 IHR. Thus, in the limited cases examined here, the 1.3 IHR always results in about 15 kt/y additional NH CH₃Br emissions.

These results remove many of the uncertainties previously associated with CH₃Br North/South interhemispheric concentration ratios and indicates that NH emissions (and thereby anthropogenic emissions) are less important than previously thought. These data also provide an important constraint on hemispheric and seasonal CH₃Br sources and sinks. Further seasonal, longitudinal, and vertical measurements are needed if the complex interactions between sources and sinks of methyl bromide are to be better understood.

Acknowledgments: This research was supported by NASA grant NAGW-452 and by an equipment grant from the W. M. Keck Foundation.

References

- Anbar, A. D., Y. L. Yung, and F. P. Chavez, Methyl bromide: Ocean sources, sinks and climate sensitivity, *Global Biogeochem. Cycles*, **10**, 175–190, 1996.
- Blake, D. R., and F. S. Rowland, Global atmospheric concentrations and source strength of ethane, *Nature*, **321**, 231–233, 1986.
- Blake, D. R., B. Sive, M. Zondlo, and F. S. Rowland, Estimate methyl bromide emissions from biomass burning, *EOS Trans. AGU*, **74**, 134, 1993.
- Blake, D. R., N. J. Blake, T. W. Smith, Jr., O. W. Wingenter, and F. S. Rowland, Nonmethane hydrocarbon and halocarbon distributions during the Atlantic Stratocumulus Transition Experiment/Marine Aerosol and Gas Exchange, June 1992, *J. Geophys. Res.*, **101**, 4501–4514, 1996.
- Blake, N. J., D. R. Blake, B. C. Sive, T.-Y. Chen, J. E. Collins, Jr., G. W. Sachse, B. E. Anderson, and F. S. Rowland, Biomass burning emissions and vertical distribution of methyl halides and other reduced gases in the South Atlantic region, *J. Geophys. Res.*, **101**, 24,151–24,163, 1996.
- Butler, J. H., and J. M. Rodriguez, Methyl bromide in the atmosphere, in *The Methyl Bromide Issue*, edited by C. H. Bell, N. Price, and B. Chakrabarti, pp. 27–90, John Wiley & Sons, Chichester, 1996.
- Cicerone, R. J., L. E. Heidt, and W. H. Pollock, Measurements of atmospheric methyl bromide and bromoform, *J. Geophys. Res.*, **93**, 3745–3749, 1988.
- Comiso, J. C., C. R. McClain, C. W. Sullivan, J. P. Ryan, and C. L. Leonard, Coastal zone color scanner pigment concentration in the Southern Ocean and relationship to geophysical surface features, *J. Geophys. Res.*, **98**, 2419–2451, 1993.
- Elliott, S. M., and F. S. Rowland, Methyl halide hydrolysis rates in natural water, *Geophys. Res. Lett.*, **20**, 1043–1046, 1993.

- Elliott, S. M., and F. S. Rowland, Nucleophilic substitution rates and solubilities for methyl halides in seawater, *J. Atmos. Chem.*, **20**, 229-236, 1995.
- Feldman, G. C., N. A. Kuring, C. Ng, W. E. Esaias, C. R. McClain, J. A. Elrod, N. Maynard, D. Endres, J. Brown, S. Walsh, M. Carle, and G. Podesta, Ocean color: Availability of the global data set, *EOS Trans. AGU*, **70**, 634-641, 1989.
- Fishman, J., J. Hoell, R. D. Bendura, W. W. J. H. Kirchhoff, and R. J. McNeal, The NASA GTE-TRACE-A Experiment (September-October, 1992), *J. Geophys. Res.*, **101**, 23,865-23,879, 1996.
- Groszko, W., and R. Moore, Ocean-atmosphere exchange of methyl bromide: NW Atlantic and Pacific Ocean studies, *J. Geophys. Res.*, in press.
- Lobert, J. M., J. H. Butler, S. A. Montzka, L. S. Geller, R. C. Myers, and J. W. Elkins, A net sink for atmospheric CH_3Br in the East Pacific Ocean, *Science*, **267**, 1002-1005, 1995.
- Lobert, J. M., S. A. Yvon-Lewis, J. H. Butler, S. A. Montzka, and R. C. Myers, Undersaturation of CH_3Br in the Southern Ocean, *Geophys. Res. Lett.*, **24**, 171-172, 1997.
- Manö, S., and M. O. Andreae, Emissions of methyl bromide from biomass burning, *Science*, **263**, 1255-1257, 1994.
- Moore R. and M. Webb, The relationship between methyl bromide and chlorophyll α in high latitude ocean waters, *Geophys. Res. Lett.*, **23**, 2951-2954, 1996.
- Penkett, S. A., B. M. R. Jones, M. J. Rycroft, and D. A. Simmonds, An interhemispheric comparison of the concentrations of bromine compounds in the troposphere, *Nature*, **318**, 550-555, 1985.
- Reeves, C. E., and S. A. Penkett, An estimate of the anthropogenic contribution to atmospheric methyl bromide, *Geophys. Res. Lett.*, **20**, 1563-1566, 1993.
- Schauffler, S. M., W. H. Pollock, and E. L. Atlas, *Proceedings of the Methyl Bromide State of the Science Workshop*, Washington, D. C., 1993.
- Shorter, J. H., C. E. Kolb, P. M. Crill, R. A. Kerwin, R. W. Talbot, M. E. Hines, and R. C. Harriss, Rapid degradation of atmospheric methyl bromide by soils, *Nature*, **377**, 717-719, 1995.
- Singh, H. B., L. J. Salas, and R. E. Stiles, Methyl halides in and over the eastern Pacific, *J. Geophys. Res.*, **88**, 3684-3690, 1983.
- Singh, H. B., and M. Kanakidou, An estimate of the anthropogenic contribution to atmospheric methyl bromide, *Geophys. Res. Lett.*, **20**, 133-136, 1993.
- Wang, C. J.-L., Global concentrations of selected halocarbons, 1988-1992, Ph. D. Dissertation, University of California, Irvine, 1993.
- Wang, C. J.-L., D. R. Blake, and F. S. Rowland, Seasonal variations in the atmospheric distribution of a reactive chlorine compound, tetrachloroethene ($\text{CCl}_2=\text{CCl}_2$), *Geophys. Res. Lett.*, **22**, 1097-1100, 1995.
- World Meteorological Organization Global Ozone Research and Monitoring Project, Report No. 37, *Scientific Assessment of Ozone Depletion: 1994*, Chapter 10, 1995.
- Yagi, K., J. Williams, N.-Y. Wang, and R. J. Cicerone, Atmospheric methyl bromide (CH_3Br) from agricultural soil fumigation, *Science*, **267**, 1979-1981, 1995.
- Yvon, S. A., and J. H. Butler, The potential effect of oceanic biological degradation on the lifetime of atmospheric CH_3Br , *Geophys. Res. Lett.*, **23**, 53-56, 1996.
- O. Wingenter, C. J.-L. Wang, D. R. Blake and F. S. Rowland, Department of Chemistry, University of California, Irvine, Irvine, California 92697-2025. (e-mail: oliver@eas.gatech.edu; cwang@cc.ncu.edu.tw; drblake@uci.edu, rowland@uci.edu)

(Received June 10, 1998; accepted June 15, 1998.)